

**UTILITY
PATENT APPLICATION
TRANSMITTAL**(Only for new nonprovisional applications
under 37 C.F.R. §1.53(b))

Attorney Docket No.

03/60-52794.1

First Inventor or Application Identifier

Koshiro Shimazu, et al.

Title

**RANEY CATALYST, PROCESS
FOR PRODUCING IT AND
PROCESS FOR PRODUCING
SUGAR-ALCOHOL USING THE
SAME**

Express Mail Label No.

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents

ADDRESS TO:

Assistant Commissioner for Patents
Box Patent Application
Washington, D.C. 20231

1. ☒ Fee Transmittal Form (e.g., PTO/SB/17)
(submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages]
(preferred arrangement set forth below)
- Descriptive title of the invention
- Cross References to Related Applications
- Statement Regarding Fed sponsored R & D
- Reference to Microfiche Appendix
- Background of the Invention
- Brief Summary of the Invention
- Brief Description of the Drawings (if filed)
- Detailed Description
- Claim(s)
- Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 1]
4. Oath or Declaration [Total Pages 3]
a. ☐ Newly executed (original or copy)
b. ☒ Copy from a prior application (37 C.F.R. §1.63(d)) (for continuation/divisional with Box 16 completed)
i. ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §1.63(d)(2) and 1.33(b).

NOTE FOR ITEMS 1 & 13. IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. §1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. §1.28).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
a. ☐ Computer Readable Copy
b. ☐ Paper Copy (identical to computer copy)
c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

7. ☐ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. §3.73(b) Statement (when there is an assignee)
☐ Power of Attorney
9. ☐ English Translation Document (if applicable)
10. ☒ Information Disclosure Statement (IDS)/PTO-1449
☐ Copies of IDS Citations
11. ☒ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503) (Should be specifically itemized)
13. ☐ Small Entity Statement(s) (PTO/SB/09-12)
☒ Statement filed in prior application, Status still proper and desired
14. ☐ Certified Copy of Priority Document(s) (if foreign priority is claimed)
15. ☐ Other: _____

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:
☐ Continuation ☒ Divisional ☐ Continuation-in-part (CIP) of prior application No: 08/743,081
Prior application information: Examiner: M. Lewis Group/Art Unit: 1754
For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

17. CORRESPONDENCE ADDRESS

- ☐ Customer Number or Bar Code Label or ☒ Correspondence address below
(insert Customer No. or Attach bar code label here)

Name	Beveridge, DeGrandi, Weilacher & Young, L.L.P.				
Address	1850 M Street, N.W., Suite 800				
City	Washington, D.C.	State		Zip Code	20036
Country	U.S.A.	Telephone	(202) 659-2811	Fax	(202) 659-1462
Name	Joseph A. DeGrandi		Reg. No.	17,446	
Signature	<i>Joseph A. DeGrandi</i>		Date	November 23, 1998	

11/23/98

0049496 44496

JC598 U.S. PTO

JC535 U.S. PTO


09/197499

11/23/98

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

FEE TRANSMITTAL Small Entity payments must be supported by a small entity statement, otherwise large entity fees must be paid. See Forms PTO/SB/09-12. See 37 C.F.R. §§1.27 and 1.28	Complete if Known	
	Application Number	Not yet assigned
	Filing Date	November 23, 1998
	First Named Inventor	SHIMAZU
	Examiner Name	Not yet assigned
	Group / Art Unit	Not yet assigned
	Attorney Docket No.	03/60-52794.1
TOTAL AMOUNT OF PAYMENT: \$380		

METHOD OF PAYMENT (check one)		FEE CALCULATION (continued)																																																																																																																																																																			
1. <input type="checkbox"/> The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to: Deposit Account No.: <u>02-4300</u> Deposit Account Name: _____ <input checked="" type="checkbox"/> Charge any additional fee Required Under 37 C.F.R. §§1.16 and 1.17 <input checked="" type="checkbox"/> Charge the Issue Fee Set in 37 C.F.R. §1.18 at the Mailing of the Notice of Allowance		3. ADDITIONAL FEES <table border="1"> <thead> <tr> <th>Large Entity Fee Code</th> <th>Large Entity Fee (\$)</th> <th>Small Entity Fee Code</th> <th>Small Entity Fee (\$)</th> <th>Fee Description</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr><td>105</td><td>130</td><td>205</td><td>65</td><td>Surcharge - late filing fee or oath</td><td></td></tr> <tr><td>127</td><td>50</td><td>227</td><td>25</td><td>Surcharge - late provisional filing fee or cover sheet</td><td></td></tr> <tr><td>139</td><td>130</td><td>139</td><td>130</td><td>Non-English specification</td><td></td></tr> <tr><td>147</td><td>2,520</td><td>147</td><td>2,520</td><td>For filing a request for reexamination</td><td></td></tr> <tr><td>112</td><td>920*</td><td>112</td><td>920*</td><td>Requesting publication of SIR prior to Examiner action</td><td></td></tr> <tr><td>113</td><td>1,840*</td><td>113</td><td>1,840*</td><td>Requesting publication of SIR after Examiner action</td><td></td></tr> <tr><td>115</td><td>110</td><td>215</td><td>55</td><td>Extension for reply within first month</td><td></td></tr> <tr><td>116</td><td>400</td><td>216</td><td>200</td><td>Extension for reply within second month</td><td></td></tr> <tr><td>117</td><td>950</td><td>217</td><td>475</td><td>Extension for reply within third month</td><td></td></tr> <tr><td>118</td><td>1,510</td><td>218</td><td>755</td><td>Extension for reply within fourth month</td><td></td></tr> <tr><td>128</td><td>2,060</td><td>228</td><td>1,030</td><td>Extension for reply within fifth month</td><td></td></tr> <tr><td>119</td><td>310</td><td>219</td><td>155</td><td>Notice of Appeal</td><td></td></tr> <tr><td>120</td><td>310</td><td>220</td><td>155</td><td>Filing a brief in support of an appeal</td><td></td></tr> <tr><td>121</td><td>270</td><td>221</td><td>135</td><td>Request for oral hearing</td><td></td></tr> <tr><td>138</td><td>1,510</td><td>138</td><td>1,510</td><td>Petition to institute a public use proceeding</td><td></td></tr> <tr><td>140</td><td>110</td><td>240</td><td>55</td><td>Petition to revive - unavoidable</td><td></td></tr> <tr><td>141</td><td>1,320</td><td>241</td><td>660</td><td>Petition to revive - unintentional</td><td></td></tr> <tr><td>142</td><td>1,320</td><td>242</td><td>660</td><td>Utility issue fee (or reissue)</td><td></td></tr> <tr><td>143</td><td>450</td><td>243</td><td>225</td><td>Design issue fee</td><td></td></tr> <tr><td>144</td><td>670</td><td>244</td><td>335</td><td>Plant issue fee</td><td></td></tr> <tr><td>122</td><td>130</td><td>122</td><td>130</td><td>Petitions to the Commissioner</td><td></td></tr> <tr><td>123</td><td>50</td><td>123</td><td>50</td><td>Petitions related to provisional applications</td><td></td></tr> <tr><td>126</td><td>240</td><td>126</td><td>240</td><td>Submission of Information Disclosure Statement</td><td></td></tr> <tr><td>581</td><td>40</td><td>581</td><td>40</td><td>Recording each patent assignment per property (times number of properties)</td><td></td></tr> <tr><td>146</td><td>790</td><td>246</td><td>395</td><td>Filing a submission after final rejection (37 CFR 1.129(a))</td><td></td></tr> <tr><td>149</td><td>790</td><td>249</td><td>295</td><td>For each additional invention to be examined (37 CFR 1.129(b))</td><td></td></tr> </tbody> </table>		Large Entity Fee Code	Large Entity Fee (\$)	Small Entity Fee Code	Small Entity Fee (\$)	Fee Description	Fee Paid	105	130	205	65	Surcharge - late filing fee or oath		127	50	227	25	Surcharge - late provisional filing fee or cover sheet		139	130	139	130	Non-English specification		147	2,520	147	2,520	For filing a request for reexamination		112	920*	112	920*	Requesting publication of SIR prior to Examiner action		113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action		115	110	215	55	Extension for reply within first month		116	400	216	200	Extension for reply within second month		117	950	217	475	Extension for reply within third month		118	1,510	218	755	Extension for reply within fourth month		128	2,060	228	1,030	Extension for reply within fifth month		119	310	219	155	Notice of Appeal		120	310	220	155	Filing a brief in support of an appeal		121	270	221	135	Request for oral hearing		138	1,510	138	1,510	Petition to institute a public use proceeding		140	110	240	55	Petition to revive - unavoidable		141	1,320	241	660	Petition to revive - unintentional		142	1,320	242	660	Utility issue fee (or reissue)		143	450	243	225	Design issue fee		144	670	244	335	Plant issue fee		122	130	122	130	Petitions to the Commissioner		123	50	123	50	Petitions related to provisional applications		126	240	126	240	Submission of Information Disclosure Statement		581	40	581	40	Recording each patent assignment per property (times number of properties)		146	790	246	395	Filing a submission after final rejection (37 CFR 1.129(a))		149	790	249	295	For each additional invention to be examined (37 CFR 1.129(b))	
Large Entity Fee Code	Large Entity Fee (\$)	Small Entity Fee Code	Small Entity Fee (\$)	Fee Description	Fee Paid																																																																																																																																																																
105	130	205	65	Surcharge - late filing fee or oath																																																																																																																																																																	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet																																																																																																																																																																	
139	130	139	130	Non-English specification																																																																																																																																																																	
147	2,520	147	2,520	For filing a request for reexamination																																																																																																																																																																	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action																																																																																																																																																																	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action																																																																																																																																																																	
115	110	215	55	Extension for reply within first month																																																																																																																																																																	
116	400	216	200	Extension for reply within second month																																																																																																																																																																	
117	950	217	475	Extension for reply within third month																																																																																																																																																																	
118	1,510	218	755	Extension for reply within fourth month																																																																																																																																																																	
128	2,060	228	1,030	Extension for reply within fifth month																																																																																																																																																																	
119	310	219	155	Notice of Appeal																																																																																																																																																																	
120	310	220	155	Filing a brief in support of an appeal																																																																																																																																																																	
121	270	221	135	Request for oral hearing																																																																																																																																																																	
138	1,510	138	1,510	Petition to institute a public use proceeding																																																																																																																																																																	
140	110	240	55	Petition to revive - unavoidable																																																																																																																																																																	
141	1,320	241	660	Petition to revive - unintentional																																																																																																																																																																	
142	1,320	242	660	Utility issue fee (or reissue)																																																																																																																																																																	
143	450	243	225	Design issue fee																																																																																																																																																																	
144	670	244	335	Plant issue fee																																																																																																																																																																	
122	130	122	130	Petitions to the Commissioner																																																																																																																																																																	
123	50	123	50	Petitions related to provisional applications																																																																																																																																																																	
126	240	126	240	Submission of Information Disclosure Statement																																																																																																																																																																	
581	40	581	40	Recording each patent assignment per property (times number of properties)																																																																																																																																																																	
146	790	246	395	Filing a submission after final rejection (37 CFR 1.129(a))																																																																																																																																																																	
149	790	249	295	For each additional invention to be examined (37 CFR 1.129(b))																																																																																																																																																																	
2. <input checked="" type="checkbox"/> Payment Enclosed: <input checked="" type="checkbox"/> Check <input type="checkbox"/> Money Order <input type="checkbox"/> Other		Other fee (specify) _____ Other fee (specify) _____ SUBTOTAL (3): \$																																																																																																																																																																			
FEE CALCULATION 1. BASIC FILING FEE <table border="1"> <thead> <tr> <th>Large Entity Fee Code</th> <th>Large Entity Fee (\$)</th> <th>Small Entity Fee Code</th> <th>Small Entity Fee (\$)</th> <th>Fee Description</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr><td>101</td><td>760</td><td>201</td><td>380</td><td>Utility filing fee</td><td></td></tr> <tr><td>106</td><td>310</td><td>206</td><td>155</td><td>Design filing fee</td><td></td></tr> <tr><td>107</td><td>480</td><td>207</td><td>240</td><td>Plant filing fee</td><td></td></tr> <tr><td>108</td><td>760</td><td>208</td><td>380</td><td>Reissue filing fee</td><td></td></tr> <tr><td>114</td><td>150</td><td>214</td><td>75</td><td>Provisional filing fee</td><td></td></tr> </tbody> </table> SUBTOTAL (1): \$380		Large Entity Fee Code	Large Entity Fee (\$)	Small Entity Fee Code	Small Entity Fee (\$)	Fee Description	Fee Paid	101	760	201	380	Utility filing fee		106	310	206	155	Design filing fee		107	480	207	240	Plant filing fee		108	760	208	380	Reissue filing fee		114	150	214	75	Provisional filing fee		SUBTOTAL (3): \$ *Reduced by Basic Filing Fee Paid																																																																																																																															
Large Entity Fee Code	Large Entity Fee (\$)	Small Entity Fee Code	Small Entity Fee (\$)	Fee Description	Fee Paid																																																																																																																																																																
101	760	201	380	Utility filing fee																																																																																																																																																																	
106	310	206	155	Design filing fee																																																																																																																																																																	
107	480	207	240	Plant filing fee																																																																																																																																																																	
108	760	208	380	Reissue filing fee																																																																																																																																																																	
114	150	214	75	Provisional filing fee																																																																																																																																																																	
2. EXTRA CLAIM FEES <table border="1"> <thead> <tr> <th>Total Claims</th> <th>Extra Claims</th> <th>Fee from below</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr><td>13 - 20** =</td><td>0</td><td>x \$0</td><td></td></tr> <tr><td>Indep. Claims</td><td>2 - 3** =</td><td>x \$0</td><td></td></tr> <tr><td>Mult. Dep</td><td></td><td></td><td></td></tr> </tbody> </table> **or number previously paid, if greater, For Reissues, see below. <table border="1"> <thead> <tr> <th>Large Entity Fee Code</th> <th>Large Entity Fee (\$)</th> <th>Small Entity Fee Code</th> <th>Small Entity Fee (\$)</th> <th>Fee Description</th> </tr> </thead> <tbody> <tr><td>103</td><td>22</td><td>203</td><td>11</td><td>Claims in excess of 20</td></tr> <tr><td>102</td><td>82</td><td>202</td><td>41</td><td>Independent claims in excess of 3</td></tr> <tr><td>104</td><td>270</td><td>204</td><td>135</td><td>Multiple dependent claim, if not paid</td></tr> <tr><td>109</td><td>82</td><td>209</td><td>41</td><td>**Reissue independent claims over original patent</td></tr> <tr><td>110</td><td>22</td><td>210</td><td>11</td><td>**Reissue claims in excess of 20 and over original patent</td></tr> </tbody> </table> SUBTOTAL (2): \$		Total Claims	Extra Claims	Fee from below	Fee Paid	13 - 20** =	0	x \$0		Indep. Claims	2 - 3** =	x \$0		Mult. Dep				Large Entity Fee Code	Large Entity Fee (\$)	Small Entity Fee Code	Small Entity Fee (\$)	Fee Description	103	22	203	11	Claims in excess of 20	102	82	202	41	Independent claims in excess of 3	104	270	204	135	Multiple dependent claim, if not paid	109	82	209	41	**Reissue independent claims over original patent	110	22	210	11	**Reissue claims in excess of 20 and over original patent																																																																																																																						
Total Claims	Extra Claims	Fee from below	Fee Paid																																																																																																																																																																		
13 - 20** =	0	x \$0																																																																																																																																																																			
Indep. Claims	2 - 3** =	x \$0																																																																																																																																																																			
Mult. Dep																																																																																																																																																																					
Large Entity Fee Code	Large Entity Fee (\$)	Small Entity Fee Code	Small Entity Fee (\$)	Fee Description																																																																																																																																																																	
103	22	203	11	Claims in excess of 20																																																																																																																																																																	
102	82	202	41	Independent claims in excess of 3																																																																																																																																																																	
104	270	204	135	Multiple dependent claim, if not paid																																																																																																																																																																	
109	82	209	41	**Reissue independent claims over original patent																																																																																																																																																																	
110	22	210	11	**Reissue claims in excess of 20 and over original patent																																																																																																																																																																	

SUBMITTED BY				Complete (if applicable)	
Typed or Printed Name	Joseph A. DeGrandi			Reg. Number	17,446
Signature		Date	November 23, 1998	Deposit Account User ID	02-4300

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THE ADDRESS, SEND TO: Assistant Commissioner of Patents, Washington, D.C. 20231.

BDW Form SED-2
Small Entity
Small Business ConcernApplicant or Patentee: (inventors) Koshiro SHIMAZU, Yoshiaki TATENO, Mitsuo MAGARA, Naoki OKAMOTO, Takao OHSHIMA, Minoru NAGASAWA and Hideki SAKAMURASerial or Patent No.: (if known) 08/743,081 Filed or Issued: (if known) November 4, 1996Atty. Dkt. No.: 03-52794For: (invention title) RANEY CATALYST, PROCESS FOR PRODUCING IT AND PROCESS FOR PRODUCING A SUGAR-ALCOHOL USING THE SAMEVERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY
STATUS (37 C.F.R. §§ 1.9(f) AND 1.27(c)) - SMALL BUSINESS CONCERN

I hereby declare that I am: (check one)

☐ the owner of the small business concern identified below:☒ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN

Nikko Rica Corporation

ADDRESS OF CONCERN

Tohoseimei Bldg., 4-4-10, Nihonbashi-muromachi, Chuo-ku, Tokyo 103, Japan

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 C.F.R. §§ 121.3-18, and reproduced in 37 C.F.R. § 1.9(d), for purposes of paying reduced fees under § 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the above-identified invention described in

(check one)

☐ the specification filed herewith☒ application Serial No. 08/743,081, filed November 4, 1996☐ patent no. _____, issued _____

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below and no rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 C.F.R. § 1.9(c) or by any concern which would not qualify as a small business concern under 37 C.F.R. 1.9(d) or a nonprofit organization under 37 C.F.R. § 1.9(e).

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 C.F.R. § 1.27)

NAME _____

ADDRESS _____

☐ INDIVIDUAL☐ SMALL BUSINESS CONCERN☐ NONPROFIT ORGANIZATION

NAME _____

ADDRESS _____

☐ INDIVIDUAL☐ SMALL BUSINESS CONCERN☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee of any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 C.F.R. § 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Hisao ISHIITITLE OF PERSON OTHER THAN OWNER PresidentADDRESS OF PERSON SIGNING c/o NIKKO RICA CORPORATION, Tohoseimei Bldg.,
4-4-10, Nihonbashi-muromachi, Chuo-ku, Tokyo 103 JAPAN

SIGNATURE _____

DATE December 27, 1996

BDW Form SED-2
Small Entity
Small Business ConcernApplicant or Patentee: (inventors) Koshira SHIMAZU, Yoshiaki TATENO, Mitsuo MAGARA, Naoki OKAMOTO, Takao OHSHIMA, Minoru NAGASAWA and Hideki SAKAMURASerial or Patent No.: (if known) 08/743,081 Filed or Issued: (if known) November 4, 1996Atty. Dkt. No.: 03-52794For: (invention title) RANEY CATALYST, PROCESS FOR PRODUCING IT AND PROCESS FOR PRODUCING A SUGAR-ALCOHOL USING THE SAME**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY
STATUS (37 C.F.R. §§ 1.9(f) AND 1.27(c)) - SMALL BUSINESS CONCERN**

I hereby declare that I am: (check one)

☐ the owner of the small business concern identified below.☒ an official of the small business concern empowered to act on behalf of the concern identified below:NAME OF CONCERN Towa Chemical Industry Co., Ltd.ADDRESS OF CONCERN 8-7, Yaesu 2-chome, Chuo-ku, Tokyo 104, Japan

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 C.F.R. §§ 121.3-18, and reproduced in 37 C.F.R. § 1.9(d), for purposes of paying reduced fees under § 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the above-identified invention described in

(check one)

☐ the specification filed herewith☒ application Serial No. 08/743,081, filed November 4, 1996☐ patent no. _____, issued _____

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 C.F.R. § 1.9(c) or by any concern which would not qualify as a small business concern under 37 C.F.R. § 1.9(d) or a nonprofit organization under 37 C.F.R. § 1.9(e).

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 C.F.R. § 1.27)

NAME _____

ADDRESS _____

☐ INDIVIDUAL☐ SMALL BUSINESS CONCERN☐ NONPROFIT ORGANIZATION

NAME _____

ADDRESS _____

☐ INDIVIDUAL☐ SMALL BUSINESS CONCERN☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee of any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 C.F.R. § 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Yoshihisa ASAITITLE OF PERSON OTHER THAN OWNER PresidentADDRESS OF PERSON SIGNING c/o TOWA CHEMICAL INDUSTRY CO., LTD., 8-7, Yaesu
2-chome, Chuo-ku, Tokyo 104 JAPAN

SIGNATURE _____

DATE December 27, 1996

Attorney Docket No.
03/60-52794.1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : SHIMAZU, et al.
Serial No. : Not yet assigned Examiner: Not yet assigned
Filed : November 23, 1998
For : RANEY CATALYST, PROCESS FOR PRODUCING IT AND
PROCESS FOR PRODUCING SUGAR-ALCOHOL USING THE
SAME

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
and Trademarks
Washington, D.C. 20231

Sir:

Prior to examination on the merits, please amend
the above-identified application as follows:

IN THE SPECIFICATION:

Page 1, before the first line, please insert
--This application is a divisional application of U.S. Appl. No.
08/743,081 filed on November 4, 1996, which is relied on and
incorporated entirely herein by reference.--

IN THE CLAIMS:

Please delete claims 2-4 without prejudice or
disclaimer.

Please add the following claims:

--5. A lump Raney catalyst for a fixed bed
catalyst made by the process comprising
melting a mixture of nickel and aluminum,
quenching droplets of said melted mixture of
nickel and aluminum to form a quenched lump alloy,

breaking said quenched lump alloy into particles,
classifying said quenched lump alloy particles by
size to obtain a range of particles having a grain diameter
suitable for forming a fixed bed catalyst,

activating said quenched lump alloy or said
quenched lump alloy particles to form a Raney catalyst.

6. The lump Raney catalyst defined in claim 5,
wherein said classified particles have a grain
diameter of approximately 2-4 mm.

7. The lump Raney catalyst defined in claim 5,
wherein said mixture consists essentially of
nickel and aluminum.

8. The lump Raney catalyst as defined in claim 7
wherein said nickel and said aluminum are present
in an amount in a range of 1:2 to 2:1 by weight.

9. A powder Raney catalyst for a fixed bed
catalyst made from the lump Raney catalyst defined in claim 5
further comprising after said activating step

crushing said Raney catalyst to form a powder.

10. A powder Raney catalyst for a fixed bed
catalyst made from the lump Raney catalyst defined in claim 7
further comprising after said activating step

crushing said Raney catalyst to form a powder.

11. A process for producing a lump Raney catalyst
for a fixed bed catalyst as defined in claim 5 comprising
melting a mixture of nickel and aluminum,

quenching droplets of said mixture of nickel and aluminum to form a quenched lump alloy,
breaking said quenched lump alloy into particles,
classifying said quenched lump alloy particles by size to obtain a range of particles having a grain diameter suitable for forming a fixed bed catalyst,
activating said quenched lump alloy made before said classifying step or activating said quenched lump alloy particles to form a Raney catalyst.

12. A process for producing a lump Raney catalyst for a fixed bed catalyst as defined in claim 6 comprising melting a mixture consisting essentially of nickel and aluminum,

quenching droplets of said mixture of nickel and aluminum to form a quenched lump alloy,
breaking said quenched lump alloy into particles,
classifying said quenched lump alloy particles to obtain a range of particles having a grain diameter of approximately 2-4 mm,
activating said quenched lump alloy made before said classifying step or activating said quenched lump alloy particles to form a Raney catalyst.

13. A process for producing a lump Raney catalyst for a fixed bed catalyst as defined in claim 7 comprising melting a mixture consisting essentially of nickel and aluminum,

quenching droplets of said mixture of nickel and aluminum to form a quenched lump alloy,

breaking said quenched lump alloy into particles,
classifying said quenched lump alloy particles to obtain a range of particles having a grain diameter suitable for forming a fixed bed catalyst,

activating said quenched lump alloy made before said classifying step or activating said quenched lump alloy particles to form a Raney catalyst.

14. A process for producing a powder Raney catalyst for a fixed bed catalyst comprising the process defined in claim 13 further comprising

crushing said Raney catalyst form a powder.

15. A process for producing a powder Raney catalyst for a fixed bed catalyst comprising the process defined in claim 11 further comprising

crushing said Raney catalyst form a powder.

16. A process for reactivating a deactivated Raney catalyst comprising

deactivating the lump Raney catalyst defined in claim 5 to form a deactivated Raney catalyst,

eluting aluminum on a surface of said deactivated Raney catalyst with an alkali to form said lump Raney catalyst.

17. A process for reactivating a deactivated Raney catalyst comprising

deactivating the powder Raney catalyst defined in claim 9 to form a deactivated Raney catalyst,

eluting aluminum on a surface of said deactivated Raney catalyst with an alkali to form said powder Raney catalyst.--

REMARKS

The specification has been amended to include the claim for priority on the parent application having U.S. Appl. No. 08/743,081.

New claims have been added to more clearly define the lump and powder Raney catalysts defined therein and a process of producing the catalysts. In addition, a process for reactivating a Raney catalyst has been included. Upon allowance of the product claims, Applicants respectfully request the Examiner to consider the process claims herein in accordance with MPEP § 821.04.

Examination on the merits is respectfully requested.

Respectfully submitted,

BEVERIDGE, DeGRANDI, WEILACHER & YOUNG, L.L.P.

By: Joseph A. DeGrandi
Joseph A. DeGrandi, Reg. No. 17,446
1850 M Street, N.W., Suite 800
Washington, D.C. 20036
Telephone: (202) 659-2811
Facsimile: (202) 659-1462

November 23, 1998

DESCRIPTION

1. Title of the Invention

Raney catalyst, process for producing it and process for producing a sugar-alcohol using the same

2. Technical Field

The present invention concerns a Raney catalyst for hydrogenation, a process for producing it and a process for producing the sugar-alcohol using the same.

3. Background Art

Actual sugar-alcohols produced industrially include sorbitol, mannitol, maltitol, xylitol and others and they are used in quantity as food additives, industrial materials or pharmaceutical materials.

In general, these sugar-alcohols are produced by the heating reaction of sugars under the hydrogen pressure in the presence of a hydrogenation catalyst.

A supported ruthenium catalyst, a Raney catalyst or the like are known as the hydrogenation catalyst used for sugar-alcohol production.

Though the supported ruthenium catalyst presents a very high catalytic activity, it provokes inconveniently sugar isomerization, decomposition and polymerization during the hydrogenation.

For solving this inconvenience, the British patent No. 867,689 describes Ru-Pd catalyst carried by activated carbon wherein ruthenium is added to palladium, however, the purity of sorbitol produced by the patent remained between 93.5 and 97.5%.

On the other hand, the Japanese TOKKYO-KOKAI-KOHO (18-month Publication of Unexamined Patent Application) SHOWA (hereinafter referred to as TOKKAISHO) 51-4370 describes Ru catalyst carried by zeolite aluminosilicate while the Japanese TOKKAISHO 51-82208 describes an example of glucose hydrogenation by Ru catalyst carried by crystalline clay

aluminosilicate, but their results were not satisfactory because the purity of sorbitol is not superior to 99% in either case.

Raney catalyst is a catalyst activated by dissolving a part of metals such as aluminum, zinc and silicon by an alkali from alloys of catalytic metals such as nickel, copper and iron and metals such as aluminum, zinc and silicon.

The catalyst presents in general a low catalytic activity and a high catalyst deterioration and the catalyst cost assumes disadvantageously a great part of the product price.

Moreover, as the catalyst is supplied mainly in powder form and used by batch method, it is necessary to provide a step for separating the catalyst from the reaction solution after the hydrogenation, the production cost increases as much.

In order to remedy this defect, a variety of Raney catalysts for fixed bed have been developed, none of them leading to a satisfactory solution.

For instance, the Japanese TOKKAISHO 50-099987 describes a method for producing a Raney catalyst for fixed bed based on nickel, cobalt or copper precipitation type catalyst.

In the method, conventional nickel, cobalt or copper precipitation type catalyst is blended and formed with powder metal/aluminum alloy and then treated at a high temperature using steam. During this step, γ - Al_2O_3 acting as binder is generated, but as the formed body is destroyed by the dissolution of γ - Al_2O_3 in the step of activation by an alkali, it is not appropriate for the production of Raney catalyst for fixed bed.

The Japanese TOKKAISHO 47-27888 describes a method for producing a Raney catalyst for fixed bed by dropping melted alloy in or on a chilled solvent to form a catalyst and activating it.

It is important to increase the density of catalyst to be loaded and to regulate the solution flow in the fixed bed for efficient hydrogenation during the sugar-alcohol production. For this sake, it is preferable to limit the catalyst grain diameter to 4 mm or less but, if the grain diameter is too small, the resistance increases and the solution flow slows

down in a way to provoke obstruction of broken catalyst, so the preferable grain diameter is 2 to 4 mm approximately.

However, if it is desirable to obtain an uniform granulating in the catalyst production, the grain diameter of this range will only be obtained in the sacrifice of the yield by the method described in the Japanese TOKKAISHO 47-27888 wherein alloy grains are produced by dropping melted metal from an orifice. Additionally, alloy grains out of this diameter range should be melted again so as to increase the cost as much.

Theretofore, the object of the present invention is to obtain a Raney catalyst for fixed bed remedying various problems mentioned hereinbefore and to produce a high purity sugar-alcohol at a low cost using the same.

4. Disclosure of this Invention

Now the present invention will be described more in detail.

In the present invention, the nickel and aluminum ratio of quenched lump alloy may be adopted between the range of 1:2 to 2:1, however, the ratio approximately 1:1 is preferable considering the alloy cost and the catalyst activity after the development.

Droplets of melted alloy are quenched forcefully by dropping into a water bath or by another way. Raney catalyst produced by activating lump alloy obtained by chilling through natural radiation may provide an initial activity but the catalyst breaks down according to the increase of use time and can not be used as fixed bed catalyst.

Preferably, droplets of melted alloy are so made to obtain their grain diameter between 1 and 15 mm after the quench.

After classification and activation as it is, the quenched lump alloy may be used as fixed bed catalyst, however, in order to increase the catalyst surface area, it is preferable that the quenched lump alloy is classified after breaking, activated and then used as fixed bed catalyst.

Either when the quenched lump alloy as it is or after break is classified, if the grain diameter is too small, it is

difficult to compose a fixed catalyst layer and even when it is composed, reaction mixture flows more slowly and it is no more possible to produce sugar-alcohol with a high productivity. On the other hand, if grains are too large, surface area per unit catalyst weight decreases so as to reduce the reaction speed and the productivity of sugar-alcohol.

To the lump form Raney catalyst according to the invention, is possible to add molybdenum, tin or the like up to 15% of catalyst metal in order to afford it with a function of its catalytic property or it is also possible to add after the activation of the catalyst.

Aqueous solution of NaOH, KOH or other alkali metal hydroxide may be used as alkali for the catalyst development and its concentration is 1 to 20%, preferably 5 to 15%. The development temperature is 40 to 100°C, preferably 60 to 85°C.

The development rate of the obtained catalyst may be determined by the following formulation after measuring the elution amount of aluminum into the alkali by means of chelatometric titration or the like.

Development rate (%) = (elution amount of aluminum / amount of aluminum in the alloy) x 100

The development rate of the lump form Raney catalyst according to the invention is 10 to 70%, preferably 15 to 60%.

The development rate is closely related to the catalyst life and the catalyst cost assumed in the sugar-alcohol production is determined by the catalyst life. The catalyst life varies according to alloy composition, kind of sugar-alcohol to be produced or others but it should assure a continuous operation.

For this sake, it is developed within the range of 10 to 70%. If the development rate is less than 10%, the expected initial activity can not be obtained and if it is higher than 70%, high initial activity is obtained but the catalyst life is shortened. This is because the catalyst becomes fragile and nickel peels off in fine powder.

The hydrogen used in the conduction of the process for producing the sugar-alcohol using the Raney catalyst according to the invention is not limited particularly, but higher purity

is more preferable.

Sugars that may be hydrogenated in the invention include glucose, xylose, maltose, lactose, fructose, starch saccharificate, sucrose or the like. They can be used alone or in combination of more than one kinds.

Normally, these sugars are supplied to the fixed bed as aqueous solution within the concentration range of 30 to 60%. If the concentration is low, the productivity will be low and if it is high, it will be difficult to eliminate reaction heat so as to deteriorate the purity of sugar-alcohol.

Material sugar is normally supplied to the fixed bed within the range of $SV=0.3$ to 1.5 .

Here, SV is determined according to the following formulation.

$SV = (\text{Material volume supplied into the reactor}) / (\text{Volume occupied by catalyst loaded into the reactor})$

Hydrogen flow rate supplied to the fixed bed is, normally, $LV=10$ to 60 m/hr and preferably $LV=15$ to 30 m/hr .

Here, LV can be determined by the following formulation:

$LV = (\text{Substance volume supplied into the reactor per unit time}) / (\text{Sectional area of the reactor})$

The reaction temperature for the conduction of the process for producing the sugar-alcohol using the Raney catalyst according to the invention varies depending on sugar-alcohols to be produced but is 110 to 150°C and preferably 120 to 145°C . The hydrogen pressure is, normally, about 40 to 200 Kg/cm^2 and preferably 50 to 150 Kg/cm^2 .

The reaction form using the lump form Raney catalyst according to the invention corresponds to the continuous reaction on the fixed bed including an upflow method wherein sugar solution is supplied from the bottom of the reactor and a downflow method wherein the same flows down from the top of the reactor and the both may be adopted equally.

The reactor shape used for this reaction may be either bath, tubular or tower type.

When the upflow method is adopted, LV of the solution flowing inside should be at least 1 m/hr and preferably 4 to 8 m/hr . LV of hydrogen is 10 to 60 m/hr and preferably 15 to 30 .

m/hr.

When the downflow method is adopted, as the hydrogen occupies more space in the reactor, the hydrogen flow might be less and the hydrogen LV is conducted within the range of 1 to 10 m/hr.

After being used for the hydrogenation of sugar under the hydrogen pressure, the lump form Raney catalyst according to the invention is collected, crushed into powder and reactivated to be reused as powder form Raney catalyst. Hence, when the present invention is conducted, the total catalyst cost may be reduced to a level lower than when the conventional powder Raney nickel catalyst is used.

The method for crushing into powder for the collected lump form Raney catalyst is not particularly limited if only powder Raney catalyst of the granuometry appropriate for the use can be obtained finally. In general, it is crushed into within the particle size of total pass through 40 mesh, preferably within the particle size of total pass through 300 mesh.

The development of powder Raney catalyst at the reactivation is conducted at the development rate of 90 to 97% under the usual conditions.

Any reaction conditions may be applied for the preparation of sugar-alcohol by the hydrogenation with the presence of powder Raney catalyst only if the purity of sugar-alcohol is not deteriorated, however, normally, the reaction is conducted with the sugar concentration of 30 to 60%, under the hydrogen pressure of at least 40 Kg/cm², preferably 50 to 150 Kg/cm² and at the temperature of 110 to 150°C.

The Raney catalyst according to the invention is a catalyst for fixed bed permitting a continuous use with a high initial activity by quenching melted alloy.

According to the process for producing the Raney catalyst of the invention, Raney catalyst, which is fixed bed catalyst, may be obtained through a short production process, without using binder for shaping, moreover, the production of the catalyst requires no special equipment.

Additionally, used lump form Raney catalyst may be collected, crushed into powder and then reactivated to be

reused.

Thus, the process for producing the sugar-alcohol using Raney catalyst according to the invention allows to produce a high purity sugar-alcohol at a low cost.

5. Brief Description of Drawings

Fig.1 is a schematic view of a hydrogenation equipment used for the conduction of the process for producing the sugar-alcohol using Raney catalyst according to the invention.

In this drawing, A refers to tower, F preheater, H refrigerator and J solution reservoir pot.

6. Description of Preferred Examples

Now the present invention will be described more in detail referring to Examples or Reference Examples which do not limit the technical scope of the invention.

Example 1:

[Production of quenched lump alloy]

6 Kg of nickel metal and 6 Kg of aluminum metal were heat-melted and dropped onto chilled water surface 20 cm below through a nozzle.

The grain diameter of the obtained quenched lump alloy was a mixture of 1 mm to 15 mm.

It was broken by a crusher and meshed to obtain 4.98 Kg of quenched lump alloy of grain diameter 2 to 4 mm.

[Development of quenched lump alloy]

34 Kg of 10% NaOH aqueous solution was poured into a 50 liter stainless container provided with heating jacket, heated to 50°C and 4.6 Kg of the quenched lump alloy contained in a stainless cage was put therein.

It was held at 60°C for 30 minutes and then the cage was lifted up and washed with water.

The development rate of lump form Raney catalyst thus obtained was 21.6%.

[Hydrogenation equipment]

Now the hydrogenation equipment used for the conduction of the process for producing the sugar-alcohol using Raney

catalyst according to the invention will be described referring to Fig. 1.

The hydrogenation equipment comprises four (4) stainless pressure vessels (inner diameter 2.1 cm, height 160 cm) of 0.5 liter with jacket connected in series and represented by A, B, C and D in the drawing, wherein a material feeding pump E is connected to the bottom of the tower A via a pre-heater F, a sampling pot I and a solution reservoir pot J are respectively connected to the top of the tower D via a refrigerator H.

Hydrogen gas enters into the bottom of the tower A, exits from the top of the tower D, is separated from solution in the solution reservoir pot J and is blown into the air through a flow meter K and regulator L.

Heated oil flows through the pre-heater F and the jacket of towers A, B, C and D to keep the temperature constant.

Normally, a valve M is open and valves N, O and P are closed and the reaction solution coming from the tower D is reserved in the pot J and discharged from a valve P from time to time.

For sampling, the valve M is closed and the valve N is opened to discharge sample from the pot I through the valve O.
[Hydrogenation reaction]

Developed lump form Raney catalyst was loaded into the reactor.

Then, respective towers were heated to 130°C and aqueous solution of 50% crystalline glucose (purity 99.7%, made by Nihon Shokuhin Kako Co., Ltd.) was supplied from the pump E at the flow rate of 2 liter/hr (SV=1).

Hydrogen was adjusted to LV=20 at 150 Kg/cm².

Hydrogenation reaction was operated continuously for 30 days and nonreducing substance in the reaction solution and purity measurement results by liquid chromatography of this period are shown in the Table 1.

Table 1

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.07	99.3
5th Day	0.10	99.2
10th Day	0.14	99.2
20th Day	0.23	99.1
30th Day	0.32	99.0

[Catalyst reuse]

After the hydrogenation reaction of 30 days, catalyst was washed with water, unloaded from respective towers and 50g of collected catalyst was crushed in the water by a crusher up to total pass through 100 mesh.

Then, 400g of 20% NaOH aqueous solution was added, stirred for one hour at 95°C and then washed with water to obtain powder Raney catalyst.

5g (as dry solid) of thus obtained powder Raney catalyst and 275g of 50% crystalline glucose aqueous solution were put into an electromagnetic stirring type autoclave of 550 ml and stirred at 130°C for 90 minutes under the hydrogen pressure of 150 Kg/cm².

At this time, the nonreducing substance in the reaction solution was 0.08%.

For reference, the nonreducing substance in the reaction solution was 0.07% when crystalline glucose was hydrogenated under the same condition using 5g of commercially available powder Raney nickel catalyst and no difference of catalytic activity was observed in comparison with the reuse of powder Raney catalyst obtained from the used lump form Raney catalyst.

Example 2:

The reaction was conducted in a similar way to the Example 1 except that 50% crystalline glucose aqueous solution was supplied as raw material at the rate of 1 liter per hour (SV=0.5) and the continuous hydrogenation was proceeded for 3 days.

The analysis results of the obtained reaction solution are

shown in the Table 2.

Table 2

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.02	99.2
Third Day	0.03	99.2

Example 3:

The reaction was conducted in a similar way to the Example 1 except that 50% xylose aqueous solution (purity 99.0%) was supplied as raw material at the rate of 1.4 liter per hour (SV=0.7) and the continuous hydrogenation was proceeded for 5 days at 120°C.

The analysis results of the obtained reaction solution are shown in the Table 3.

As the results show, the catalyst prepared by the method of the Example 1 was able to be used satisfactorily for the hydrogenation of xylose.

Table 3

Reaction time	Nonreducing substance (%)	Xylitol purity (%)
First Day	0.05	98.4
Third Day	0.09	98.2
5th Day	0.17	98.1

Example 4:

The reaction was conducted in a similar way to the Example 1 except that 50% maltose aqueous solution (purity 95.2%, made by Nihon Shokuhin Kako Co., Ltd.) as raw material was supplied at the rate of 1.2 liter per hour (SV=0.6) and the continuous hydrogenation was proceeded for 5 days at 135°C.

The analysis results of the obtained reaction solution are shown in the Table 4.

As the results show, a constant purity maltitol has been produced for 5 days continuous hydrogenation without remarkable increase of nonreducing substance.

Table 4

Reaction time	Nonreducing substance (%)	Maltitol purity (%)
First Day	0.04	94.9
Third Day	0.06	94.9
5th Day	0.07	94.9

Example 5:

The reaction was conducted in a similar way to the Example 1 except that 50% aqueous solution of starch hydrolysate (TN-55, made by Japan Corn Starch Co., Ltd.) as raw material was supplied at the rate of 1.4 liter per hour (SV=0.7) and the continuous hydrogenation was proceeded for 5 days at 145°C.

The composition of the used starch hydrolysate was glucose 2.2%, maltose 53.6%, maltotriose 19.1%, tetrasaccharide or more 25.1%.

The analysis results of the obtained reaction solution are shown in the Table 5.

Using the catalyst prepared according to the method of the Example 1, even raw material containing much component of relatively high molecular weight such as trisaccharide or more could be hydrogenated continuously.

Table 5

Reaction time	First Day	Third Day	5th Day
Nonreducing substance (%)	0.09	0.13	0.18
Sugar-alcohol composition of reaction solution (%)			
Sorbitol	2.2	2.3	2.2
Maltitol	54.2	54.0	53.8
Maltotriitol	18.4	18.7	18.9
Hydrogenated tetrasaccharide or more	25.1	25.0	25.1

Example 6:

The reaction was conducted in a similar way to the Example

1 except that 40% lactose aqueous solution as raw material was supplied at the rate of 1.6 liter per hour (SV=0.8) and the continuous hydrogenation was proceeded for 3 days at 140°C.

The analysis results of the obtained reaction solution are shown in the Table 6.

Table 6

Reaction time	Nonreducing substance (%)	Lactitol purity (%)
First Day	0.03	99.2
Third Day	0.04	99.2

Example 7:

The reaction was conducted in a similar way to the Example 1 except that 40% crystalline fructose aqueous solution as raw material was supplied at the rate of 1.6 liter per hour (SV=0.8) and the continuous hydrogenation was proceeded for 3 days at 125°C.

The analysis results of the obtained reaction solution are shown in the Table 7.

Table 7

Reaction time	First Day	Third Day
Nonreducing substance (%)	0.05	0.07
Sorbitol (%)	51.4	51.3
Mannitol (%)	48.2	48.3
Others (%)	0.4	0.4

Example 8:

The reaction was conducted in a similar way to the Example 1 except that 50% sugar aqueous solution as raw material was supplied at the rate of 2.4 liter per hour (SV=1.2) and the continuous hydrogenation was proceeded for 3 days at 160°C.

The analysis results of the obtained reaction solution are shown in the Table 8.

Table 8

Reaction time	First Day	Third Day
Nonreducing substance (%)	0.04	0.05
Sorbitol (%)	75.0	75.0
Mannitol (%)	24.2	24.3
Others (%)	0.8	0.7

Example 9:

[Hydrogenation equipment]

The hydrogenation equipment used for this Example is not illustrated but it concerns an equipment similar to the hydrogenation equipment of Fig. 1, wherein the raw material feeding pump E is connected to the top of the tower A through the pre-heater F, the sampling pot I and the solution reservoir pot J are respectively connected to the bottom of the tower D through the refrigerator H.

In the equipment, the bottom of the tower A was connected to the top of the tower B, the bottom of the tower B to the top of the tower C and the bottom of the tower C to the top of the tower D respectively.

Thus, the hydrogenation equipment used for this Example is similar to the hydrogenation equipment of the Example 1 shown in Fig. 1 except that the hydrogen gas enters into the top of the tower A and exits from the bottom of the tower D.

[Hydrogenation reaction]

In the Example 1, the reaction was conducted in a similar way to the Example 1 except that 50% crystalline glucose aqueous solution as raw material was supplied at the rate of 1 liter per hour (SV=0.5) and the continuous hydrogenation was proceeded with the hydrogen flow rate of 2 liters per hour.

The analysis results of the obtained reaction solution are shown in the Table 9.

Table 9

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.07	99.3
5ht Day	0.09	99.3
10th Day	0.11	99.1

Example 10:

34 Kg of 10% NaOH aqueous solution was poured into a 50 liter stainless container provided with heating jacket and heated to 60°C.

4.6 Kg of quenched lump alloy of grain diameter 2 to 4 mm produced in a way similar to the Example 1 and contained in a stainless cage was put into the said aqueous solution of NaOH.

It was held at 80°C for 2 hours and then the cage was lifted up and washed with water.

Here, the catalyst development rate was 40.8%.

This catalyst was loaded into an equipment similar to the one of the Example 1 and crystalline glucose was hydrogenated under the similar hydrogenation conditions.

The analysis results thereof are shown in the Table 10.

Compared to the Example 1, glucose could be hydrogenated continuously for a long time even when the catalyst development rate was increased to 40.8%.

Moreover, the destruction of catalyst was not observed.

Table 10

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.05	99.3
5th Day	0.08	99.3
10th Day	0.18	99.1
20th Day	0.46	98.8
30th Day	0.72	98.7

Example 11:

55 Kg of 15% NaOH aqueous solution was poured into a 50 liter stainless container provided with heating jacket and

heated to 60°C.

4.6 Kg of quenched lump alloy of grain diameter 2 to 4 mm produced in a way similar to the Example 1 and contained in a stainless cage was put into the said aqueous solution of NaOH.

It was held at 80°C for 2.5 hours and then the cage was lifted up and washed with water.

Here, the catalyst development rate was 58.9%.

This catalyst was loaded into an equipment similar to the one of the Example 1 and crystalline glucose was hydrogenated under the similar hydrogenation conditions.

The analysis results thereof are shown in the Table 11.

Compared to the Example 1, if the catalyst development rate was increased to 58.9%, the catalyst activity decreased rather rapidly during the continuous operation but within a satisfactory range from the view point of industrial used because it did not provoke the destruction of catalyst.

Table 11

<u>Reaction time</u>	<u>Nonreducing substance (%)</u>	<u>Sorbitol purity (%)</u>
First Day	0.05	99.3
5th Day	0.26	99.1
10th Day	0.48	98.7
20th Day	1.20	98.1

Example 12:

25 Kg of nickel metal and 25 Kg of aluminum metal were heat-melted and dropped onto chilled water surface 20 cm below through a nozzle.

The grain diameter of thus obtained quenched lump alloy was within the range of 1 to 15 mm. It was screened by a sieve to obtain 6.2 Kg of quenched lump alloy of grain diameter 2 to 4 mm.

34 Kg of 10% NaOH aqueous solution was poured into a 50 liter stainless container provided with heating jacket, heated to 60°C and 4.6 Kg of the quenched lump alloy contained in a stainless cage was put therein.

It was held at 80°C for 25 minutes and then the cage was

lifted up and washed with water.

The development rate of catalyst thus obtained was 22.4%.

The reaction was conducted in similar hydrogenation conditions to the Example 1 except that the obtained lump form Raney catalyst was loaded into the same equipment as the Example 1 and 50% glucose was supplied at the rate of 1.2 liter per hour (SV=0.6).

The analysis results thereof are shown in the Table 12.

As the results show, the quenched lump form catalyst of the invention could hydrogenate sugars even when it was activated as it is without break.

Then, after a continuous operation of 30 days, the catalyst was collected, powdered and developed in a similar way to the Example 1 before hydrogenating crystalline glucose once more.

Here, the nonreducing substance was 0.08% and the catalyst activity was within the satisfactory range.

Table 12

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.06	99.1
5th Day	0.09	99.1
10th Day	0.12	99.1
20th Day	0.26	98.8
30th Day	0.38	98.7

Example 13:

Quenched lump alloy obtained in the Example 12 was screened by a sieve to obtain 8.6 Kg of quenched lump alloy of grain diameter 4 to 8 mm.

34 Kg of 10% NaOH aqueous solution was poured into a 50 liter stainless container provided with heating jacket, heated to 60°C and 4.6 Kg of said quenched lump alloy contained in a stainless cage was put therein.

It was held at 80°C for 120 minutes and then the cage was lifted up and washed with water.

The development rate of catalyst thus obtained was 38.6%.

The hydrogenation was conducted in similar conditions to the Example 1 except that this catalyst was loaded into the same equipment as the Example 1 and 50% glucose was supplied at the rate of 0.8 liter per hour (SV=0.4).

The analysis results thereof are shown in the Table 13.

The catalyst activity was satisfactory even when the grain diameter of catalyst was prepared to 4 to 8 mm.

Table 13

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.06	99.0
5th Day	0.10	99.0
10th Day	0.15	98.9
20th Day	0.32	98.7
30th Day	0.64	98.5

Reference Example 1:

6 Kg of nickel metal and 6 Kg of aluminum metal were heat-melted, poured onto a metal plate and left there.

The obtained alloy was broken by a crusher and screened through a sieve to obtain 5.3 Kg of alloy within the grain diameter range of 2 to 4 mm.

34 Kg of 10% NaOH aqueous solution was poured into a 50 liter stainless container provided with heating jacket and heated to 60°C.

4.6 Kg of the alloy contained in a stainless cage was put into the said NaOH aqueous solution. It was held at 60°C for 30 minutes and then the cage was lifted up and washed with water.

The development rate of catalyst thus obtained was 23.8%.

Crystalline glucose was hydrogenated under the similar conditions as the Example 1 except that this catalyst was used, however, the reaction was suspended as the nonreducing substance increased suddenly at the 5th day.

Moreover, broken powder catalyst was observed in the reaction solution.

The analysis results of this are shown in the Table 14.

Table 14

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.56	98.8
5th Day	1.26	98.2

Reference Example 2:

55 Kg of 15% NaOH aqueous solution was poured into a 50 liter stainless container provided with heating jacket and heated to 60°C.

4.6 Kg of quenched lump alloy made by the same method as the Example 1 and contained in a stainless cage was put into the NaOH aqueous solution.

It was held at 80°C for 4 hours and then the cage was lifted up and washed with water.

The development rate of catalyst thus obtained was 73.8%.

Crystalline glucose was hydrogenated by the same method as the Example 1 except that this catalyst was used; when the solution has been supplied for 10 days, the reaction was suspended as broken catalyst obstructed the equipment.

The analysis results of this are shown in the Table 15.

Table 15

Reaction time	Nonreducing substance (%)	Sorbitol purity (%)
First Day	0.05	99.3
5 th Day	0.18	99.2
10th Day	0.86	98.7

CLAIMS

1. A powder type Raney catalyst obtained by using for the hydrogenation under the hydrogen pressure a lump form Raney catalyst made by (i) the first step for melting nickel and aluminum, (ii) the second step for obtaining quenched lump alloy by quenching droplets of said melted mixture and (iii) the third step for classifying and activating said quenched lump alloy as it is or once it is broken, collecting said lump form Raney catalyst, crushing into powder and reactivating.

2. A process for producing the powder type Raney catalyst comprising the steps of:

using for the hydrogenation under the hydrogen pressure a lump form Raney catalyst made by (i) the first step for melting nickel and aluminum, (ii) the second step for obtaining quenched lump alloy by quenching droplets of said melted mixture and (iii) the third step for classifying and activating said quenched lump alloy as it is or once it is broken, collecting said lump form Raney catalyst, crushing into powder and reactivating.

3. A process for producing the sugar-alcohol characterized by: using the lump form Raney catalyst made by (i) the first step for melting nickel and aluminum, (ii) the second step for obtaining quenched lump alloy by quenching droplets of said melted mixture and (iii) the third step for classifying and activating said quenched lump alloy as it is or once it is broken, and hydrogenating sugars under the hydrogen pressure.

4. A process for producing the sugar-alcohol characterized by: using the powder type Raney catalyst made by using for the hydrogenation under the hydrogen pressure a lump form Raney catalyst made by (i) the first step for melting nickel and aluminum, (ii) the second step for obtaining quenched lump alloy by quenching droplets of said melted mixture and (iii) the third step for classifying and activating said quenched lump alloy as it is or once it is broken, collecting said lump

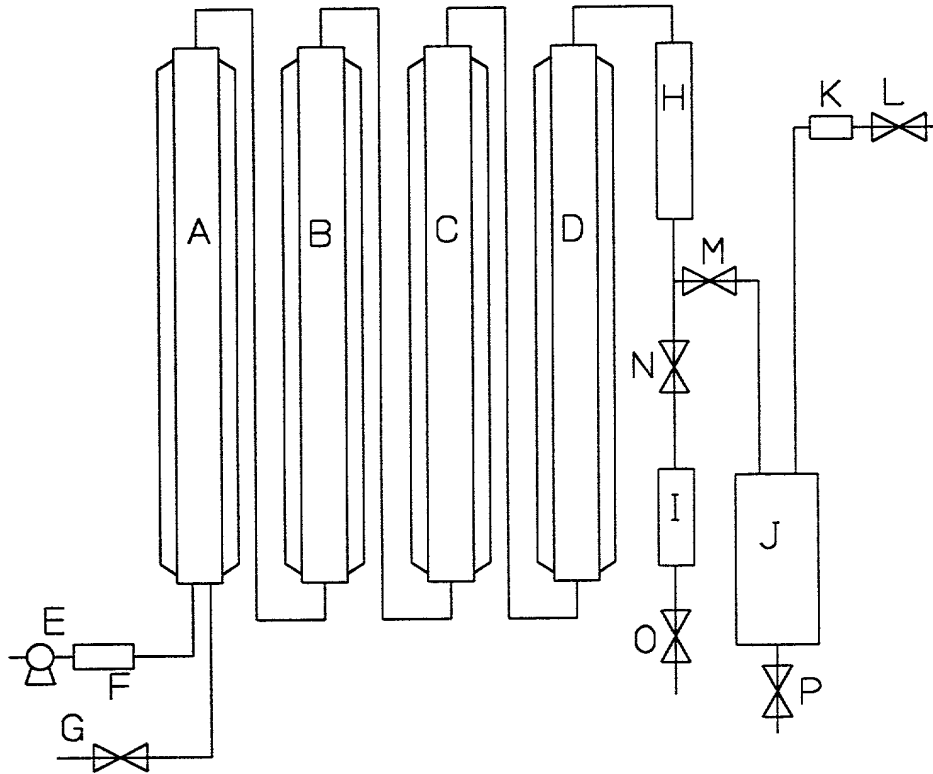
form Raney catalyst, crushing into powder and reactivating, and hydrogenating sugars under the hydrogen pressure.

ABSTRACT

To obtain a Raney catalyst for fixed bed permitting a continuous use with a high initial activity and to produce a high purity sugar-alcohol at a low cost using the same.

For this object, sugar-alcohol is produced by:
using the powder type Raney catalyst made by using for the hydrogenation under the hydrogen pressure a lump form Raney catalyst made by (i) the first step for melting nickel and aluminum, (ii) the second step for obtaining quenched lump alloy by quenching droplets of said melted mixture and (iii) the third step for classifying and activating said quenched lump alloy as it is or once it is broken, collecting said lump form Raney catalyst, crushing into powder and reactivating, and hydrogenating sugars under the hydrogen pressure.

FIG. 1



Declaration and Power of Attorney United States Patent Application

UNITED STATES (Form BDWY-1,
Patents and Design Patents
Sole & Joint Inventor:
Convention & Non-convention:
PCT & Non-PCT
This form cannot be amended, altered
or changed after it is signed
(For use only for inventors who
understand the English language.)

Attorney Docket No.: 03-52794

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled RANEY CATALYST, PROCESS FOR PRODUCING IT AND PROCESS FOR PRODUCING A SUGAR-ALCOHOL USING THE SAME, the specification of which

(check one) ☐ is attached hereto.

☒ was filed as U.S. Application No. 08/743,081 on November 4, 1996 and (if applicable) was amended on _____.

☐ was filed as PCT International Application No. on _____ and (if applicable) was amended under PCT Article 19 on _____.

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §§ 119(a)-(d) or § 365(b) of any foreign and PCT application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America listed in this Declaration. I have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application(s) on which priority is claimed:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)
7-313,720	Japan	November 8, 1995	YES

I hereby claim the benefit under Title 35, United States Code, § 120 or § 365(c) of any United States application and PCT international application designating the United States of America listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

I hereby claim priority benefits under Title 35 United States Code § 119(e) of any U.S. provisional application(s) listed below:

U.S. Provisional Application No.	Filing Date

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Joseph A. DeGrandi (17446), Robert G. Wellacher (20531), Richard G. Young (20628), Michael A. Makuch (32263), Dennis C. Rodgers (32936), Thomas L. Evans (35805) and Maurice U. Cahn (30454).

Send all correspondence to Beveridge, DeGrandi, Wellacher & Young, L.L.P., Suite 800, 1850 M Street, N.W., Washington, D.C. 20036. Facsimiles may be sent to (202) 659-1462. Direct all telephone calls to (202) 659-2811.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor:

Koshiro SHIMAZU

Citizenship: Japan

Residence (city, state, country):

Shizuoka, Japan

Post office address:

3589-12, Imaizumi, Fuji-shi, Shizuoka 417 JAPAN

Signature: Koshiro Shimazu

Date: December 27, 1996

☒ Additional inventors and/or prior applications are listed in attached Supplemental Sheet(s).

BDWY 995

Supplemental Sheet to U.S. Declaration and Power of Attorney

(BDWY-1 supp.)

Additional Inventor(s):

I hereby declare that all statements made in the attached Declaration and Power of Attorney of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of second joint inventor, if any: Yoshiaki TATENO Citizenship: Japan
 Residence (city, state, country): Shizuoka, Japan
 Post office address: 1333-55, Aisuhara, Fuji-Shi, Shizuoka 419-01 Japan
 Signature: Yoshiaki Tateno Date: December 27, 1996

Full name of third joint inventor, if any: Mitsuo MAGARA Citizenship: Japan
 Residence (city, state, country): Shizuoka JAPAN
 Post office address: 61-18, Nekoya, Numazu-shi, Shizuoka 410-03, Japan
 Signature: Mitsuo Magara Date: December 27, 1996

Full name of fourth joint inventor, if any: Naoki OKAMOTO Citizenship: Japan
 Residence (city, state, country): Chiba, Japan
 Post office address: 4-61-17, Minamihanashima, Matsudo-Shi, Chiba 271 JAPAN
 Signature: Naoki Okamoto Date: December 27, 1996

Full name of fifth joint inventor, if any: Takao OHSHIMA Citizenship: Japan
 Residence (city, state, country): Saitama, Japan
 Post office address: 8-33, Mukaimachi, Gvoda-shi Saitama 361, Japan
 Signature: Takao Oshima Date: December 27, 1996

Full name of sixth joint inventor, if any: Minoru NAGASAWA Citizenship: Japan
 Residence (city, state, country): Saitama, Japan
 Post office address: 4-9-3, Tsuji, Urawa-shi, Saitama 336, Japan
 Signature: Minoru Nagasawa Date: December 27, 1996

Full name of seventh joint inventor, if any: Hideki SAKAMURA Citizenship: Japan
 Residence (city, state, country): Gunma, Japan
 Post office address: 1695-2, Hanetsuku, Tatebayashi-shi, Gunma 374, Japan
 Signature: Hideki Sakamura Date: December 27, 1996

Additional Foreign/PCT Applications:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)

Additional U.S. Applications:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

Additional Provisional U.S. Applications:

U.S. Provisional Application No.	Filing Date